

PATENT ABSTRACTS OF JAPAN

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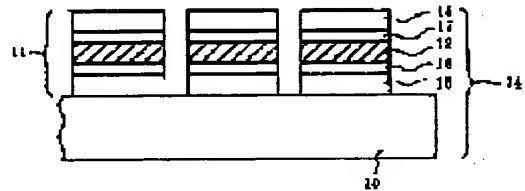
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(54) ELECTRODE SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an electrode substrate free from trouble in the connection of electrodes in spite of low electrical resistance and high moisture resistance by varying the concn. of indium or tin in the thickness direction of multiple oxide thin films.

SOLUTION: The multiple oxide thin films 15 to 18 on at least one side where a silver alloy thin film 12 is held consists of two layers varying in the concn. of the indium or tin and are so disposed that the concn. of the indium or tin of the multiple oxide 15, 18 on the outermost layers not in contact with the silver alloy thin film 12 is made higher. The conductive film formed on the electrode substrate 10 is usable as a transparent electrode having high transmittance by forming the thinner film thickness of the silver alloy thin film 12 held by the multiple oxides 15 to 18. Conversely, the conductive film is usable as a reflection electrode having high reflectivity by forming the thicker film thickness of the silver alloy thin film 12. The reflection electrode is usable as the electrode of a liquid crystal display device of a reflection type and electroluminescence(EL).



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CLAIMS

[Claim(s)]

[Claim 1] The electrode substrate characterized by the concentration of an indium or tin differing in the thickness direction of a mixed oxide thin film in the electrode substrate equipped with the electric conduction film of a configuration of pinching a silver alloy thin film with the mixed oxide thin film which uses indium oxide or the tin oxide as a base material on a substrate.

[Claim 2] The electrode substrate according to claim 1 characterized by arranging so that it may consist of two layers which pinch a silver alloy thin film, and from which the concentration of an indium or tin differs [the mixed oxide thin film of one side] at least and the indium of the mixed oxide of the outermost layer or the concentration of tin may become high.

[Claim 3] The electrode substrate according to claim 1 or 2 with which thickness of a silver alloy thin film is characterized by being in the range of 7-25nm.

[Claim 4] The electrode substrate according to claim 1 or 2 with which thickness of a silver alloy thin film is characterized by being in the range of 50 to 200 nm.

[Claim 5] The electrode substrate according to claim 1, 2, 3, or 4 with which a silver alloy thin film is characterized by being the silver alloy which added gold, copper, palladium, or one or more sorts of platinum to silver.

[Claim 6] The electrode substrate according to claim 1, 2, 3, 4, or 5 with which a mixed oxide thin film is characterized by containing cerium oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the substrate which is used for output display units, such as liquid crystal display equipment and plasma display equipment, the I/O display which performs a direct input from the display screen, or a solar battery and with which the transparent electrode was formed, or the electrode substrate with which the reflector was formed.

[0002]

[Description of the Prior Art] The electrode substrate with which the transparent electrode of the electrode configuration which penetrates a visible ray was prepared on substrates, such as glass and plastic film, is widely used for the electrode for a display of various displays (display screen), such as liquid crystal display equipment, the I/O electrode which can carry out a direct input from the display screen of this display.

[0003] Moreover, in the liquid crystal display of a reflective mold, while faces a transparent electrode and, as for a reflector, the adoption is being considered as an electrode of light reflex nature. as a transparent electrode, the thin film of ITO which is the mixed oxide which added the tin oxide uses for indium oxide widely -- having -- **** -- the specific resistance -- about -- It is 2×10^{-4} ohm-cm. Moreover, **** of ITO When it is 200nm, the sheet resistivity becomes 10ohms / **.

[0004] although powerful ITO a little also began to be marketed from this in recent years -- the sheet resistivity -- thickness 300nm -- it is -- abbreviation 5ohm/** -- it is -- specific resistance -- about -- It is 1.5×10^{-4} ohm-cm.

[0005] On the other hand, in the 7thICVM held in Japan, the transparence electric conduction film of a three-tiered structure constituted by the front rear face of a silver thin film as heat ray reflective film by carrying out the laminating of an ITO thin film or the indium oxide thin film (IO thin film) is proposed in 1982. the transparence electric conduction film of this three-tiered structure -- about -- It has sheet resistivity with low 5ohms / ** extent, and the application to the above-mentioned transparent electrode was expected taking advantage of that high conductivity.

[0006] by the way, in the above-mentioned display unit or an I/O device, increasing a pixel consistency and displaying a precise screen in recent years is called for, and the eburnation of the above-mentioned transparent electrode pattern requires in connection with this -- having -- **** -- for example, -- It is required that the terminal area of the above-mentioned transparent electrode should be constituted from a pitch which is about 100 micrometers.

[0007] Moreover, in liquid crystal display equipment, in the method (COG method) with which IC for a liquid crystal drive is directly connected to a substrate, there is a part from which length **** of wiring serves as a thin line called width of face of 20-50 micrometers, and the advanced etching processing suitability which is not in the former, and high conductivity (low resistivity) are demanded.

[0008] Moreover, on the other hand, enlargement of the display screen is also called for. In order to form the transparent electrode of a precise pattern which was mentioned above in such

formation of a large-sized screen and to enable it to impress sufficient driver voltage for liquid crystal moreover, the transparent electrode equipped with the high conductivity below 4.5ohms / **, as the above-mentioned transparent electrode needed to be applied.

[0009] Moreover, in the liquid crystal display of the passive-matrix drive method which used STN LCD etc. in addition to this, when performing the multi-gradation display of 16 or more gradation, low sheet resistivity is demanded of the pan below 3ohm/**.

[0010] however, the transparent electrode of the above-mentioned three-tiered structure proposed in the 7thICVM -- also setting -- at most -- The sheet resistivity of 5ohms / ** extent did not pass to be obtained, but there was a problem that sufficient conductivity was not securable. In addition, it can be said by making thickness of the silver thin film of the transparent electrode of the above-mentioned three-tiered structure thick to about 16-18nm that it is possible to reduce the sheet resistivity to about 3ohms / **. However, when thickness of a silver thin film is thickened, visible-ray permeability (especially wavelength about 610nm long wave visible-ray permeability by the side of merit) falls to about 75%, and the problem that the function as a transparent electrode will be spoiled arises.

[0011] Furthermore, in the transparent electrode of the above-mentioned three-tiered structure, i.e., the laminated structure of ITO and a silver thin film, it is easy to produce a reaction under existence of moisture, and easy to bring about silver condensation and destruction of ITO especially focusing on the interface. the silverfish which can be easily checked by looking as a result -- the fault that the defect of a ** arises and a display defect, an open circuit of a transparent electrode, etc. arise -- **** -- it is.

[0012]

[Problem(s) to be Solved by the Invention] this invention persons are Japanese Patent Application No., in order to cancel the low moisture resistance which was a problem in the laminated structure of ITO and a silver thin film. The technique shown in No. 88797 [seven to] was proposed. Since this technique, i.e., moisture resistance, and transmission are raised, the transparence electric conduction film of high moisture resistance can be obtained with the technique used as the silver alloy which used the mixed oxide as the mixed oxide which added cerium oxide etc. to indium oxide, and added copper etc. to silver in the silver alloy.

[0013] It is necessary to add cerium oxide about 10 to 40% with the configuration by this technique, for example for damp-proof improvement and the improvement in permeability. However, with the configuration which pinches the thin film of a silver alloy with the mixed oxide which added much cerium oxide, the conductivity of the oxide thin film which is a mixed oxide falls greatly to indium oxide.

[0014] Consequently, as a drive electrode of a liquid crystal display, surface electrical resistance became high and the electrical installation to TAB (film which processed the copper circuit pattern into the polyimide film) etc. became very unstable.

[0015] This invention is made in view of such a trouble, and the place made into the technical problem is located in the place which provides connection of an electrode with the inconvenient electrode substrate which is not, though it is high moisture resistance in low resistance.

[0016]

[Means for Solving the Problem] this invention persons propose making the oxide layer of high moisture resistance arrange to the field side which arranges a conductive high oxide layer in the field side which inquires wholeheartedly that the above-mentioned technical problem should be solved, consequently performs electrical installation with TAB etc. as above-mentioned The means for solving a technical problem, and touches a silver alloy thin film. The presentation ratio of indium oxide or the tin oxide which is rich in conductivity is low set up with the oxide of the side which touches a silver alloy thin film, and, more specifically, is highly set up with an outside oxide.

[0017] That is, invention concerning claim 1 is characterized by the concentration of an indium or tin differing in the thickness direction of a mixed oxide thin film in the electrode substrate equipped with the electric conduction film of a configuration of pinching a silver alloy thin film with the mixed oxide thin film which uses indium oxide or the tin oxide as a base material on a substrate.

[0018] Moreover, invention concerning claim 2 is characterized by arranging so that the indium of the mixed oxide of the outermost layer which consists of two layers which pinch a silver alloy thin film, and from which the concentration of an indium or tin differs [the mixed oxide thin film of one side] at least, and does not touch a silver alloy thin film, or concentration of tin may be made high.

[0019] The electric conduction film currently formed in the electrode substrate of this invention can be used as a transparent electrode with high permeability by forming thinly the thickness of the silver alloy thin film currently pinched with the mixed oxide. Moreover, conversely, by forming the thickness of a silver alloy thin film thickly, it can be used as a reflector with a high reflection factor, and a reflector can be used as the liquid crystal display of a reflective mold, and an electrode of electroluminescence (EL).

[0020] Namely, invention of claim 3 relates to a transparent electrode, and is the thickness of a silver alloy thin film. It is characterized by considering as the range of 7-25nm. Moreover, claim 4 Invention is characterized by making thickness of a silver alloy thin film into the range of 50 to 200 nm with respect to a reflector.

[0021] The thickness of a silver alloy thin film as a transparent electrode When not fulfilling 7nm, a silver alloy thin film turns into film of discontinuity, and cannot turn into continuous homogeneous film easily. Moreover, it becomes the transparent electrode in which an optical property and conductivity were inferior. Furthermore, although the thickness of a silver alloy thin film serves as [in / at the thickness which is 25nm / the light wave length of 550 nm] a transparent electrode of the permeability around 80%, if this is exceeded greatly, permeability becomes low and is not desirable as a transparent electrode.

[0022] Moreover, a silver alloy thin film is a reflector. Although you may form by the thickness exceeding 200nm, since the reflection factor of light does not become higher than this, it is not necessary to set it up thickly more than 200nm, even if it sets it as the thickness exceeding 200 nm.

[0023] If a silver alloy thin film is formed with the silver alloy which added noble metals, such as gold, copper, palladium, and platinum, to silver, it can make the dependability of the electric conduction film of three layers which pinches a silver alloy thin film with a mixed oxide improve. for example, the addition of the above-mentioned noble metals -- 5at% (atomic percent) -- if it is the following, without having big effect on the light transmittance (or rate of a light reflex) of the electric conduction film, or conductivity; it has high-reliability and high adhesion with a substrate, and the electric conduction film of 3 lamination can be offered.

[0024] That is, invention concerning claim 5 is characterized by being the silver alloy with which the silver alloy thin film added one or more sorts of gold, copper, palladium, and platinum to silver.

[0025] Moreover, in order to raise the adhesion force with oxide further, transition metals, such as metals, such as a metaled indium, tin, aluminum, and magnesium, and nickel, may be added to a silver alloy small quantity (for example, less than [2at%]).

[0026] the addition of the gold to silver, copper, palladium, and platinum was mentioned above -- as -- the range with little effect to an optical property (light transmittance or rate of a light reflex), or conductivity which is not -- it is -- total amount 6at% (atomic percent) -- the following is desirable. In addition, since full dissolution of the gold is carried out with silver, even if it adds to about 20at%, it cannot have so big effect on an optical property easily. the addition to the silver of these noble metals, and about [0.3at%] small quantity -- even when -- although effectiveness begins to be seen -- from a viewpoint of damp-proof improvement -- respectively -- in order more than 0.5at% is desirable and to secure low sheet resistivity (high conductivity) -- respectively -- Less than [3at%] is desirable.

[0027] Indium oxide and the tin oxide which are a good conductor at the base material of the mixed oxide of the both sides of a silver alloy thin film by the electric conduction film of 3 lamination which pinches a silver alloy thin film are desirable. Although a zinc oxide may be used as a base material, acid resistance and since it is inferior in respect of alkali resistance, front 2 persons are desirable.

[0028] Moreover, it is desirable to add the oxide of semimetals, such as an oxide of lanthanum

system metals, such as an oxide of transition metals high-melting [, such as Ti, Zr, Hf, Nb, Ta, and Cr,] and Ce, and Bi, germanium, Si, etc. to said base material in order to raise the moisture resistance of the electric conduction film of 3 lamination. Also in it, since especially the addition to the base material of cerium oxide (CeO₂) combines high chemical resistance and a high refractive index, it is desirable. That is, invention of claim 6 is that are characterized by containing cerium oxide, and a mixed oxide thin film makes a mixed oxide thin film contain cerium oxide, and considers as a high refractive index, and can raise permeability as a transparent electrode.

[0029] In addition, it is good for the base material of indium oxide or the tin oxide also as a mixed oxide thin film which added the metallic oxide mentioned above besides cerium oxide.

[0030] making the rate of the cerium in a base material into 1 - 50at% (atomic percent), when adding cerium oxide to the indium oxide which is a base material -- desirable -- especially -- 3 - 40at% is desirable. That is, when cerium oxide is added exceeding 40at(s)% to a base material, in processing of the sputtering target used for membrane formation of a mixed oxide thin film, it is to become easy to generate a crack at a target.

[0031] In addition, while asking for the rate of the cerium oxide in a base material by following (several 1) (several 1) (Ce element) (In element), description is the atomic percent (at%) of a cerium element and an indium element respectively, and both make the oxygen element no count.

[0032]

[Equation 1]

$$\text{セリウムの割合 (at\%)} = \frac{(\text{Ce 元素})}{(\text{Ce 元素} + \text{In 元素})} \times 100$$

[0033] The electrode substrate of this invention can be used for all as an electrode substrate for displays of a transparency mold or a reflective mold. For example, when using as an electrode substrate for indicating equipments of a reflective mold, the substrate which forms an electrode may be the transparence or the opaque substrate colored other colors, such as transparent substrates, such as glass and plastics, or white, and black. Furthermore, the substrate itself may be a substrate with which semiconductor devices, such as an electrical circuit, a solar battery or an amorphous silicon, polish recon, and MIM (diode component), were formed, or it may be a substrate with optical functions, such as a polarizing element, a diffraction grating, light-scattering film, lambda/4 plate, or a phase contrast film. Furthermore, you may be the substrate which formed the color filter beforehand.

[0034] Moreover, since the electric conduction film of 3 lamination of this invention is low resistance, it can be used for signal lines, bus lines, etc. of a component, such as TFT (thin film transistor) and MIM (diode component), and it can also be used also [electrodes / these / pixel].

[0035]

[Embodiment of the Invention] Below, the example of the operation gestalt of this invention is explained at a detail based on a drawing.

[0036] As shown in <example 1> drawing 1 , the electrode substrate 14 of the transparency mold concerning this (example 1) Thickness The 1st layer mixed oxide 15 (34nm of thickness) of the tin-oxide base material by which the laminating was carried out one by one on the 0.7mm glass substrate 10, and the 2nd layer mixed oxide 16 (thickness 8nm), the silver alloy thin film 12 (16nm of thickness) -- the principal part consists of a 3rd layer mixed oxide 17 (thickness 8nm) and a 4th layer mixed oxide 18 (37nm of thickness) further.

[0037] Here, this (example 1) 1st layer mixed oxide 15 and 3rd layer mixed oxide 17 have added indium oxide to the tin oxide which is a base material. namely, metal tin and metal indium conversion (let an oxygen element be no count) -- it is -- respectively -- tin 99at% (atomic percent) and indium the tin oxide made into 1at% (atomic percent) -- it is considering as the rich (there are many amounts of the tin oxide) presentation. In addition, at this (example 1), the addition oxide to a mixed oxide is indium oxide. Although considered as 1at%, it changes into this, and they are an initial complement, in addition ***** about other dopants, such as

antimony oxide.

[0038] Moreover, the 2nd layer mixed oxide 16 and the 4th layer mixed oxide 18 are metallic element conversions (let an oxygen element be no count), and used cerium oxide and an oxidation gallium as the mixed oxide of gallium 10at% of presentation cerium 10at% tin 80at% at the tin-oxide base material, respectively. Furthermore, the silver alloy thin film 12 is silver 97at% and gold. 2at%, copper It considered as the silver alloy of 1at% of presentation.

[0039] Subsequently, the transparent electrode 11 of the configuration of the five above-mentioned layers is formed in the following manufacture processes. That is, the resist pattern of a negative pattern configuration was first formed in the front face (field side which forms a transparent electrode 11 in drawing 1) of the washed glass substrate 10 by the technique of the usual photolithography.

[0040] Subsequently, laminating membrane formation of the 1st layer mixed oxide, the 2nd layer mixed oxide, a silver alloy thin film, the 3rd layer mixed oxide, and the 4th layer mixed oxide was continuously carried out on the glass substrate 10 in the vacuum with the sputtering system. In addition, in case each class is formed, membranes are formed by adjusting the amount of the oxygen gas introduced into equipment.

[0041] Subsequently, after picking out the glass substrate 10 from the sputtering system and irradiating ultraviolet-rays light all over said resist pattern, the resist pattern was removed using the frilling liquid of an organic alkali system, and it considered as the pattern of a transparent electrode 11. To after an appropriate time and a glass substrate 10 Heat treatment of 1 hour was performed at 220 degrees C, and it considered as the electrode substrate 14.

[0042] In this way, the sheet resistivity of the obtained electrode substrate 14 is about 3ohm/**, and is sum total thickness. The specific resistance calculated by 103nm is abbreviation. It turned out that it has 3.1×10^{-5} ohm-cm and very good conductivity. Moreover, wavelength The light transmittance in 550nm was about 94%.

[0043] When the mounting test was performed to the transparent electrode on this (example 1) electrode substrate 14 through the anisotropy electric conduction film which distributed the metal particle of nickel for the film (it has the 480 wiring sections) with which a copper circuit pattern is called TAB by which processing formation was carried out at a polyimide film, the defective continuity in 480 wiring parts was not seen, but had got good electrical installation.

[0044] <Example 1 of a comparison> Subsequently to drawing 3 , for the comparison with the above (example 1), the electrode substrate 34 was formed so that it might be shown. In that case, it adds to the tin oxide which is a base material so that it may become gallium 10at% of presentation cerium 10at% tin 80at%, and cerium oxide and an oxidation gallium are used for it as a mixed oxide. The above-mentioned mixed oxide is used and it is thickness in the almost same manufacture process as (an example 1). On the 0.7mm glass substrate 30, the transparent electrode 31 of 3 lamination was formed by carrying out laminating membrane formation of the mixed oxide layer 36 (42nm of thickness), the silver alloy thin film 32 (16nm of thickness), and the mixed oxide layer 37 (45nm of thickness) one by one, and it considered as this (example 1 of a comparison) electrode substrate 34.

[0045] Like the above (example 1), when the mounting test in TAB is performed to the electrode substrate 34 of (the example 1 of a comparison), it is close under wiring connection of 480, and to an abbreviation moiety. 225 defective continuity occurred.

[0046] the electrode substrate 24 of the reflective mold concerning [as shown in <example 2> drawing 2] this (example 2) -- thickness the 1st layer mixed oxide 25 (20nm of thickness) by which the laminating was carried out one by one on the 0.7mm glass substrate 20, and the silver alloy thin film 22 (thickness 120nm) -- it is further with the 2nd layer mixed oxide 27 (10nm of thickness), and the 3rd layer mixed oxide 28 (65nm of thickness), and the principal part is constituted.

[0047] Here, the 1st layer mixed oxide 25 and the 2nd layer mixed oxide 27 have added cerium oxide, the tin oxide, and titanium oxide to the indium oxide used as a base material. Moreover, the presentation of a mixed oxide is indium 76.5at% and cerium 20at% and tin, respectively at the atomic percent (let an oxygen element be no count) of metallic element conversion. 3at%, titanium It may be 0.5at%. Moreover, cerium oxide, the tin oxide, and titanium oxide are added

also to the 3rd layer mixed oxide 28 which uses indium oxide as a base material, and the presentation of a mixed oxide is indium 92.5at% and a cerium, respectively at the atomic percent (let an oxygen element be no count) of metallic element conversion. 5at%, tin 3at%, titanium It may be 0.5at%.

[0048] Subsequently, the reflector 21 of the 4 above-mentioned lamination was formed in the following manufacture processes. First, after the surfactant and water of an organic alkali system washed the front face of the washed glass substrate 20, it held in the vacuum tub (sputtering system), and after performing plasma treatment called reverse sputtering, washing processing of the front face was carried out further. Next, a glass substrate 20 was not taken out out of the vacuum tub, but laminating membrane formation of the 1st layer mixed oxide, a silver alloy thin film, the 2nd layer mixed oxide, and the 3rd layer mixed oxide was carried out one by one on the glass substrate 20 by the sputtering method do not heat.

[0049] Subsequently, after forming the resist pattern (positive pattern) of a reflector configuration by the technique of photolithography on the reflector 21 of the 4 above-mentioned lamination, the outcrop besides a pattern was etched with the sulfuric-acid-nitric-acid system etching reagent. Subsequently, the resist frilling back, and 220 degree C and annealing (heat treatment) of 1 hour were performed, and it considered as the reflector 24.

[0050] In this way, the sheet resistivity of the obtained reflector 21 was about 0.28ohm/**. Moreover, sum total thickness It became the specific resistance calculated as 215nm, and 6.0×10^{-6} ohm-cm.

[0051] When the mounting test was performed to the polyimide film on the reflector 21 of this (example 2) electrode substrate 24 through the anisotropy electric conduction film with which the copper circuit pattern distributed the metal particle of nickel using the film (it has the 480 wiring sections) called TAB by which processing formation was carried out, the defective continuity in 480 wiring parts was not seen, but good electrical installation was obtained.

[0052] <Example 2 of a comparison> Subsequently to drawing 4, for the comparison with (an example 2), the electrode substrate 44 was formed so that it might be shown. In that case, it is metallic element conversion (let an oxygen element be no count) about cerium oxide and titanium oxide at the indium oxide which is a base material, respectively, and they are indium 76.5at% and cerium 20at% and tin. 3at%, titanium It adds so that it may become 0.5at% of presentation, and it uses as a mixed oxide. The above-mentioned mixed oxide is used and it is thickness in the almost same manufacture process as (an example 1). On the 0.7mm glass substrate 40, the transparent electrode 41 of 3 lamination was formed by the 1st layer mixed oxide 46 (20nm of thickness), the silver alloy thin film 42 (120nm of thickness), and carrying out laminating membrane formation one by one, and carrying out the 2nd layer mixed oxide 47 (75nm of thickness) further, and it considered as this (example 2 of a comparison) electrode substrate 44.

[0053] this (example 2 of a comparison) -- having mentioned above (example 2) -- when the mounting test in TAB was similarly performed, under wiring connection of 480 and six defective continuity occurred.

[0054]

[Effect of the Invention] According to this invention, as compared with the transparent electrode called the conventional ITO in the oxide of an electrode surface important for connection by mounting, it can consider as the electric conduction film with specific resistance with single figure - double good figures by making the presentation ratio of a conductive high oxide high. That is, an electrode substrate with high practical use level with sufficient mounting nature of an electrode and high moisture resistance can be offered. Moreover, application large as an antireflection film, the electromagnetic wave shielding film or the transparent electrode for solar batteries, and reflective film can do the electrode substrate of this invention by adjusting selection of a substrate ingredient, and the thickness of a mixed oxide thin film and a silver alloy thin film, and it can be said that this invention is excellent practically.

[0055]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The explanatory view showing one example of the electrode substrate of this invention.

[Drawing 2] The explanatory view showing other examples of the electrode substrate of this invention.

[Drawing 3] The explanatory view showing an example of the conventional electrode substrate.

[Drawing 4] The explanatory view showing other examples of the conventional electrode substrate.

[Description of Notations]

10, 20, 30, 40 Substrate

11 31 Transparent electrode

21 41 Reflector

14, 24, 34, 44 Electrode substrate

12, 22, 32, 42 Silver alloy thin film

15, 16, 17, 18 Mixed oxide

25, 27, 28 Mixed oxide

36, 37, 46, 47 Mixed oxide

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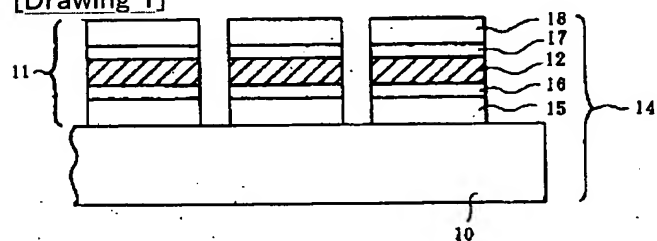
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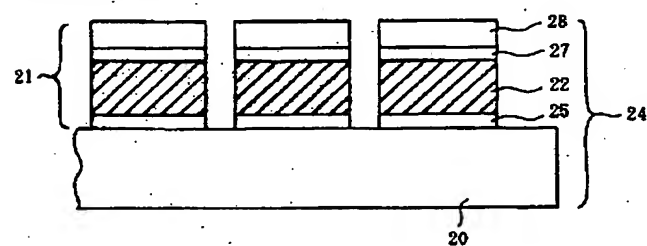
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DRAWINGS

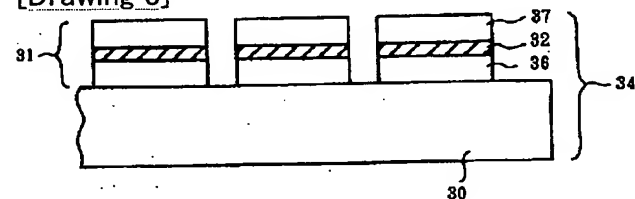
[Drawing 1]



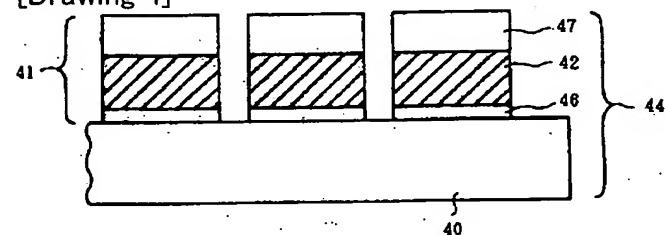
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]